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FREEZE DRYING

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CHAPTER VII

FREEZE DRYING

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The average monthly production of penicillin in the United States during 1943 amounted to 1.7×10^9 Oxford units. Corresponding figures for 1944 and 1945 were 138×10^9 and 570×10^9, respectively (*33*). This remarkable accomplishment amid the restrictions and shortages of World War II stands as an objective tribute to American ingenuity and productivity (*10*). The statistics reflect the results of integrated effort ranging from applied research—such as that which led to a spectacular increase in the yield of penicillin during fermentation—to the design and construction of multimillion dollar plants. It must also be recalled that during the cited period penicillin was inactivated by moderate temperatures, by acids and bases, by moisture, by heavy metals, by primary alcohols, by oxidizing agents, and by penicillinase, the last being concurrently produced during fermentation (*30*). At one step in the recovery process, penicillin had a rate of deterioration at 0°C. corresponding to a half-life of 2.5 hours. Substantial losses were incurred during purification even though the commercial product, as produced in the spring of 1944, still contained more than 50 percent water-soluble impurities. At this time FDA regulations required penicillin to be dated for use in 6 months or less, notwithstanding another requirement for storage at temperatures below 10°C. (*9*). In view of the lability of penicillin, it is not surprising that freeze drying was the preferred method for minimizing damage during the drying operations. Dehydration imparted sufficient stability to the penicillin of the mid 1940's to ensure its effectiveness in the battle zones throughout the world and in the hospitals at home and abroad.

STABILIZATION OF PENICILLIN

Before the initiation of the penicillin program the delicacy of freeze drying had been well established from experience with such heat-sensitive materials as blood plasma, enzymes, viable bacteria and viruses, many types of immune sera, and histological preparations. Experience with the drying of blood plasma in the United States and England early in World War II had demonstrated the feasibility of freeze drying on a commercial scale. Earl Flosdorf (*12*) in the United States and R. I. N. Greaves (*18*) of England deserve recognition for outstanding contributions which carried the freeze drying of blood plasma from a laboratory operation to a successful commercial process. This experience with plasma was a major factor in expediting the commercial production of penicillin.

Freeze drying, also called *lyophilization* and *sublimation drying*, is characterized by the elimination of water as vapor directly from the ice phase of the frozen product. In reality, freezing results in the separation of water in the form of "pure" ice crystals. During freeze drying these ice crystals are removed by sublimation. As a preliminary requirement for freeze drying, the aqueous phase must be solidly frozen. Professor Greaves (*17*) has emphasized that the term *freeze drying* should be reserved for the procedure in which drying takes place below the lowest eutectic temperature after precautions have been taken to assure the absence of a metastable, glassy component.

For freeze drying to progress at a feasible rate, heat must be supplied to the subliming ice. For steady state drying, heat input must provide the heat of sublimation, which is equal to the combined heats of vaporization and of fusion of water, and whatever additional heat is required to adjust the vapor to the temperature of the sublimation environment. Moreover, the vapor resulting from sublimation must escape from the immediate vicinity of the ice, through whatever layer of dry material is present, and be removed from the system. This removal can be effected by direct pumping, by condensation on a refrigerated surface, or by trapping with a desiccant. As a practical means of accelerating the mobility of water vapor, the drying chamber is maintained at a pressure well below the triple point. Also, in the production of penicillin for parenteral use, elaborate precautions are necessary to assure the sterility of the final product and the reliability of its ultimate container.

The focal point of freeze drying systems, like those widely installed in the United States for penicillin production, was an insulated chamber of the type shown in Figure 1. One wall of this chamber was a hinged door providing access to a tier of ten to twelve hollow shelves or platens, each approximately 13 square feet. The temperature of the platens could be controlled from

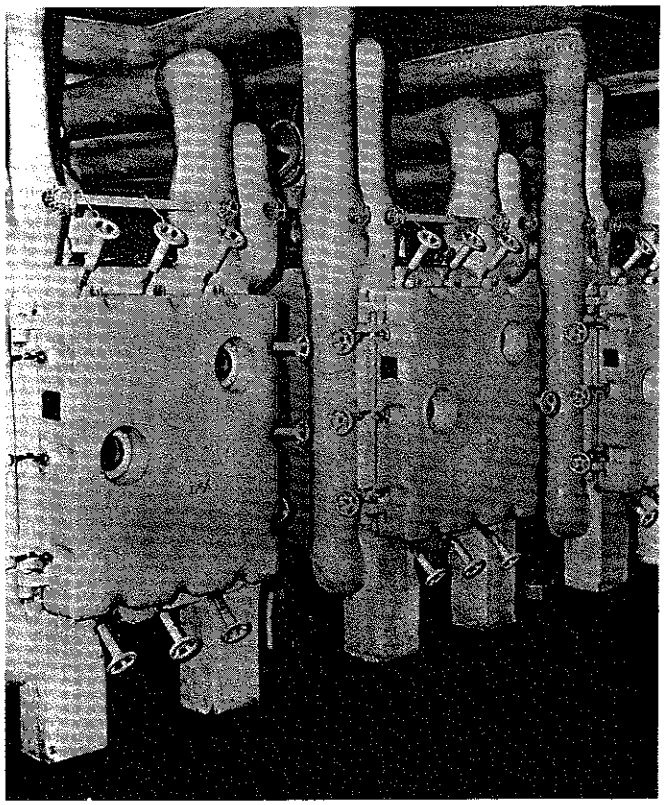

Fig. 1. Freeze drying chambers for penicillin, 1945 (courtesy of Stokes Equipment Division, Pennsalt Chemicals Corporation).

about −40° to +80°C. by circulating fluid from external refrigeration and heating units through the tortuous internal structure of the platens. The chamber with its internal and external fittings was designed to maintain a vacuum of a few microns and to withstand sterilization with direct steam at pressures corresponding to 120°C.

Vacuum was developed either with a multistage steam ejector or with a mechanical pump operating in series with a refrigerated condenser which was designed to operate at −60°C. or lower. Several large installations introduced a jet diffusion pump between the refrigerated condenser and the mechanical pump (*8*).

At the start of the drying cycle, trays loaded with frozen penicillin solution, either in bulk or in small bottles (ampoules or vials), were transferred to the platens of the drying chamber. The platens were precooled to about −30°C. to prevent thawing during the period required to pump the chamber to an operating pressure within the range 0.1 to 0.6 torr, which corresponds to the vapor pressure of ice at −40° to −22.6°C. At such pressures the presence of a liquid phase resulted in damage due to foaming. As previously noted, the commercial penicillin of the mid-1940's contained a high percentage of water-soluble impurities, which sometimes gave rise to eutectic points below −30°C. To avoid foaming such lots required cautious processing after application of the full refrigeration potential of the platens.

After the chamber had been evacuated to operating pressure, the temperature of the platens was gradually increased to accelerate drying. Theoretically the freeze drying phase ends when all the ice has sublimed. Further drying, commonly called *secondary drying*, is necessary to attain a residual moisture of one percent, which is regarded as essential for maximum stability. Secondary drying involves the removal of "bound," or "adsorbed," moisture which remains unfrozen owing to its low vapor pressure. To dry to one percent moisture requires the application of higher temperatures; fortunately, by the time the ice has been sublimed, the penicillin can withstand a substantially higher temperature for a brief period without damage.

As an additional complicating factor, penicillin had to be freeze dried in standardized unit doses in bottles, from which it was reconstituted for injection. This requirement was met by transferring a precise volume, generally 5 or 10 ml., of standardized solution, sterilized by filtration, to a 20- to 25-ml. bottle. Bottles were packed upright in trays, frozen, and thence transferred to the chilled platens of the drying chamber. In 1942–3 T. K. Sherwood directed a group of investigators on a project which identified and evaluated the major factors affecting the rate of freeze drying of penicillin from bottles under the conditions cited above. Sherwood's contributions have been summarized by Flosdorf (*12*). In part these studies showed that heat transfer to the zone of sublimation determined the overall length of the drying cycle. The most important factor affecting this transfer is the resistance offered by the insulating layer of dry penicillin formed during drying. On the other hand, factors affecting the flow of vapor from the ice zone to the chamber had a negligible effect on the drying time. Professor Sherwood developed operating procedures for drying penicillin from bottles. He was the first to use a shielded ice cube with an embedded thermocouple for measuring the vapor pressure of water in the chamber. His most important contribution, however, was his approach to the elucidation of the mechanisms involved in freeze drying.

During the mid-1940's a small but increasing amount of penicillin was freeze dried in bulk in trays. While this practice facilitated drying operations, it added to the problem of assuring sterility, especially during subsequent operations in which standardized amounts of dry penicillin were weighed into individual bottles. Aside from the problem of maintaining sterility, the fact that the penicillin was exceedingly hygroscopic necessitated elaborate humidity control in the working area.

In 1948 a procedure became available for the recovery of a high-purity crystalline penicillin with a markedly improved stability. Freeze drying consequently was no longer required in commercial production. The experience gained in the freeze drying of both blood plasma and penicillin, however, taught that freeze drying was not restricted to laboratory operations and encouraged

commercial exploitation beyond the limits imposed by the pharmaceutical industry.

BACKGROUND FOR THE FREEZE DRYING OF FOOD

Among the potential applications for freeze drying, food has received the greatest attention. Flosdorf's exploratory observations on fruit juices and milk took place as early as 1935, and during the following decade his observations were extended to raw meats, oysters, fish fillets, soups, corned beef, fruits, vegetables, and coffee extract (*11*, *12*). At the Low Temperature Research Station, a few minutes' walk from Professor Greaves's laboratory at Cambridge University, experiments were performed in 1939 on the quality and storage characteristics of freeze dried peas (*2*). Many investigations performed during the 1940's and early 1950's revealed the superiority of freeze dried foods over similar items which had been dehydrated by historic methods.

Freeze drying is applicable to virtually all foods, both raw and cooked, which are suitable for preservation by freezing and particularly to skeletal muscle, vegetables, and fruits, for which the retention of normal structure is essential. Except for a practical limit of about three-fourths inch in thickness, there is no restriction on the size or shape of the food mass to be dried. The sublimation of ice crystals from the rigidly frozen state causes no shrinkage and results in a highly porous structure favorable to the penetration of water during rehydration. Freeze dried foods generally rehydrate within 15 minutes, to yield products which in flavor, texture, appearance, and nutritional quality closely simulate corresponding products which have been frozen but not dried. Dehydration provides a reliable method of preservation against all types of microbiological deterioration. In addition, dehydration results in a reduction in weight ranging from 50 to 90 percent, depending on the food.

Recognition of the preceding advantages must be tempered by the knowledge that all foods are susceptible to damage during the drying process and to deteriorative changes in subsequent handling and storage. However, when properly prepared and protected by adequate packaging, most freeze dried foods are rated as acceptable even after storage for 12 months at 38°C.; few canned foods receive a comparable rating under such conditions. The most formidable deterrent to increased commercial production of freeze dried foods is the added cost of processing. In contrast to the freeze drying of high-priced pharmaceutical products, for which the weight of a unit dose is hardly significant, food is a low-cost, high-tonnage commodity for which competitively priced alternatives are generally available.

The above considerations provide a strong stimulus for research and development on freeze dried foods, on specialized processes and equipment for their production, and on physical mechanisms underlying the drying process. A significant part of this stimulus has stemmed from the United States Army in recognition of the unique advantages of freeze dried products in areas where refrigeration is nonexistent or unreliable. In time of war this area embraces all regions outside the continental United States. A cursory survey of citations in several review articles shows the increasing interest in the freeze drying of foods. Flosdorf's book published in 1949 is a comprehensive survey of freeze drying theory and all its recognized applications. Two sections of this book, titled "Food Applications" and "Equipment for Food," cover a total of twenty-three pages and include eight literature citations. A review article directed exclusively to the freeze drying of food was published by Harper and Tappel in 1957 (*21*); this article carries sixty-five references. In 1964 Burke and Decareau (7) updated and extended Harper and Tappel's review; 155 articles were cited. As further evidence of professional vigor, between 1954 and 1966 there were six international conferences on freeze drying at which food was the primary or a major issue.

THEORY AND APPLICATION OF FREEZE DRYING TO FOODS

Pretreatment of foods destined for freeze drying requires operations normally performed on commercially frozen foods, including formulation and cooking in the case of frozen convenience items. Notwithstanding substantial investigation of the freezing of fruits and vegetables (*22*) and of animal tissues (*25*), the commercial freezing of food before freeze drying does not differ essentially from the comparable operation in the frozen food industry. Freezing to an arbitrary temperature or to a rigid state is not an infallible guide to adequate freezing. It is important that the food be frozen below the lowest eutectic point and that metastable states be eliminated. Rey and Bastien (*31*) have demonstrated the sensitivity of electrical resistance measurements for identifying incomplete freezing or incipient melting. The same authors point to the usefulness of differential thermal analysis for determining eutectic temperatures. The preceding reference to "incomplete" freezing does not apply to bound or adsorbed water, which in animal and plant products usually amounts to 0.2 to 0.3 gram/gram of dry solids (*24*). It is this type of water which is removed during secondary drying after the ice phase has disappeared.

From the strictly physical standpoint, freeze drying can be treated as a series of heat and mass transfers joined through a phase transition at the ice interface. Figure 2 is a schematic representation of the basic elements of a freeze drying system and of the sequential recession of the ice which initially is dispersed throughout

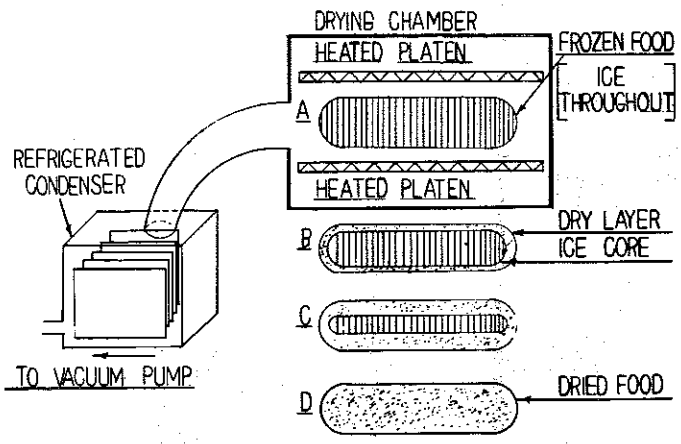

Fig. 2. Schematic freeze drier with food masses representing the initial (A), intermediate (B,C), and final (D) stages of drying.

the food mass (see *A*), with the concurrent increase in the thickness of the dry layer as drying progresses (see *B*, *C* and *D*).

The pressure exerted by water-vapor molecules in equilibrium with ice is dependent upon temperature. For water molecules to escape from the restrictions imposed by the crystal lattice of ice into the unrestricted vapor phase requires energy corresponding to the heat of sublimation. This heat is withdrawn from the ice with the escaping vapor, and, if it is not restored, the decreased temperature of the ice results in a reduced vapor pressure and a corresponding reduction in rate of sublimation. To illustrate the relationship among temperature, vapor pressure, and total pressure of the system in their effect upon the rate of sublimation, I have assumed that the frozen food mass *A* in Figure 2 has a substantial amount of superficial ice, that the chamber, platens, and food mass are at −10°C., and that the refrigerated condenser is at −30°C. The total pressure, P, in the chamber is equal to the sum of the partial pressures of the air, p_a, and water vapor, p_w. At atmospheric pressure the difference in vapor pressure between ice at the food surface (1.95 torr) and ice on the refrigerated condenser (0.29 torr) provides the driving force for the diffusion of vapor from the surface of the food to the condenser. Transfer, however, is exceedingly slow owing to the resistance to diffusion provided by the 2.8×10^{19} molecules in each cubic centimeter of stagnant air between the ice and the condenser. When the pressure in the chamber is reduced to 1 torr, as is usual in the freeze drying of food, most of the air is swept from the chamber, and p_w approaches P. Under such conditions the resistance caused by stagnant air becomes negligible, and the rate of sublimation limited by other factors. At a chamber pressure of 1 torr the temperature of the ice cannot exceed −17.3°C. Adjustment to the lower temperature is achieved by sublimation cooling, which theoretically withdraws about 680 calories/gram of vapor lost. Maintaining a steady rate of sublimation requires the introduction of heat to stabilize the temperature and hence the vapor pressure of the ice. In the freeze drying of food the sublimation of ice gives rise to a shell of dry solids which increases in thickness as sublimation progresses. This dry shell (see Figure 2, *B* and *C*) resists both the transfer of heat to the ice zone and the escape of vapor from the vicinity of the ice to the surface of the food. As pointed out by Burke and Decareau (7) the theory underlying the movement of water vapor through this dry shell is complex and suffers from a lack of experimental data. This deficiency is gradually being compensated for by programs such as those undertaken by Sandall (*32*) and Hardin (*20*), who have described the rate of drying in relation to measurable parameters.

Far more experimental effort has been directed to heat transfer during freeze drying than to mass transfer. In recognition of current commercial practice, Figure 2 shows frozen food as oriented between heated platens, since radiation is presumed to be the primary mechanism of heat transfer to the food surface. Reliance on radiation in place of conduction has resulted in a reduction of almost 50 percent in the time required for a freeze drying cycle; however, the higher temperatures employed have increased the risk of heat damage to the dry surface. In the literature of freeze drying, recognition has been given to the possibility that radiant heating is affected by the absorptivity and emissivity of the food being dried, but such measurements have not been correlated with the rate of freeze drying. Burgheimer (6) suggests that the very near infrared (0.8 to 1.0 micron) favors more rapid drying than do longer wavelengths.

Burke and Decareau (7) pointed out that the former practice of placing food in trays which are in direct contact with the heated platens generally fails to provide uniform heating, due to incomplete contact between the tray and the platen and between the food and the tray. The difficulty in achieving efficient conduction of heat to the product is emphasized by the development of equipment for accelerated freeze drying at the Experimental Factory of the British Ministry of Agriculture, Fisheries and Food (*19*). This process requires a chamber with movable platens which press expanded aluminum mesh several millimeters into the food during the drying process, thereby achieving the intimate contact required for conduction.

As pointed out by Oetjen, et al. (*29*), and supported by observations of Burke and Decareau (7), convection may be important in the transfer of heat to the food being dried at pressures between 0.5 and 2.0 torr.

Radio-frequency energy offers an attractive potential for transmitting the heat of sublimation directly to the ice, but a review by Burke and Decareau (7) covering a number of investigations suggests that commercial feasibility based on existing equipment is improbable.

Whether heat is supplied to the exterior of the dry food by radiation, conduction, or convection, transfer through

the dry layer to the ice surface depends on conduction. Owing to their highly porous structure, freeze dried foods have a thermal conductivity comparable to that of the best insulating materials. In addition, a substantial decrease in thermal conductivity occurs when the food is measured at reduced pressure such as that used in freeze drying. A reduction in chamber pressure from 2.0 to 0.1 torr may decrease thermal conductivity of the dry layer by seven eighths. Such calculations favor the use of higher chamber pressures provided there is adequate control to avoid melting. This principle provides the basis for a patent by Mellor (*27*) which claims to effect a marked reduction in freeze drying time through cyclic changes in chamber pressure. The increased thermal conductivity at elevated pressure is enhanced when helium is used to elevate pressure.

Triebes and King (*34*) found that freeze-dried turkey muscle is anisotropic, thermal conductivity parallel to the grain being 60 to 80 percent greater than that normal to the grain.

Brynko and Smithies (*5*) circumvented the thermal resistance of the dried layer by impaling food on metal spikes which conduct heat directly to the ice zone.

In the freeze drying of food, curves for residual moisture in relation to time of drying show a rapid initial rate, often virtually constant, which gradually lapses into a prolonged period of decreasing rate. Roughly one third of the total drying time is required for reducing the moisture from around 0.2 to 0.02 gram/gram of dry solids. It is generally accepted that this difficult-to-remove moisture is of the bound, adsorbed, or capillary type and, owing to restrictive forces, was never frozen (*24*). There appears to be no precise transition between freeze drying and secondary drying. Sandall (*32*) estimated that during freeze drying there is a transition in the adsorbed moisture of the dry shell ranging from 0.3 gram/gram of dry solids at the subliming interface to approximately 0.02 gram at the surface of the dry shell.

In spite of the importance of secondary drying to food stability, little experimental effort has been directed toward reducing the time or the temperature requirements, but, as noted by Burke and Decareau (7), the application of microwave heating to accelerate secondary drying may prove commercially feasible.

EQUIPMENT FOR FREEZE-DRYING FOOD

The systems currently used in the United States for the freeze drying of food differ little in principle from those employed in the production of penicillin two decades ago. Provision is generally made for radiant heat transfer from heated platens in place of conductive transfer. The instrumentation, control, and programming of the system have become more sophisticated. The main area of progress, however, has been toward greater size of equipment and toward labor economy. Figure 3 shows a recent installation designed specifically for the freeze drying of food.

The features of freeze drying equipment currently used for commercial production are reviewed by Burke and Decareau (7). This review also covers the essential features of the drier with moveable platens as developed by the British (*19*) and the German equipment controlled by the tempamatic process.

Within the past five years there has been considerable interest in freeze drying at atmospheric pressure or at pressures substantially above the triple point. These processes utilize a cold, dry gas to remove water vapor from the frozen food and also to supply the heat of sublimation. Engineers at the FMC Corp. (*13*) have used a readily condensible, water-immiscible carrier such as *n*-heptane or hexane. Operating temperatures and pressures are selected to maintain the food in the frozen state and to avoid condensation of the vapor on the food.

A relatively inexpensive continuous freeze drier suitable for pilot plant production has been assembled at the Western Regional Laboratory of the U.S. Department of Agriculture. Several commercial semicontinuous freeze driers have been fabricated by Leybold in Germany. These driers provide for the transfer of dry product to a reliable container without exposure to atmospheric oxygen and humidity.

Greaves (*17*) described his experience with the design and operation of a spray freeze drier, which can be applied only to essentially structureless foods such as milk, fruit juices, and tea and coffee extracts. The FMC Corp. (*14*) has been granted a United States patent on a spray freeze drying system designed primarily for coffee.

According to the literature on freeze drying, vapor is removed from the drying chamber by a refrigerated condenser, steam ejectors, or chemical desiccants. In practice, however, very little use has been made of desiccants during the drying operation. In a United States patent, Graham, Brown, and Ramage (*15*) describe a novel application of silica gel for freeze drying bacterial pellets. In a cited example a dispersion of bacterial cells containing about 10 percent solids was frozen as one-eighth-inch pellets by being dropped into a bath of refrigerant. The pellets were mixed in a refrigerated vessel evacuated to 0.1 torr with four times their weight of silica gel. After about 4 hours the moisture content of the pellets was reduced to 10 percent. Pellets were separated with a sieve. Repetition of the above treatment reduced the moisture content to one percent. In a following patent Graham, Brown, and Ramage (*16*) indicated the applicability of the silica gel process to fruits, vegetables, meat, fish, eggs, and other foods. A serendipitous feature of the process is the fact that the heat of adsorption of silica gel is very near the heat

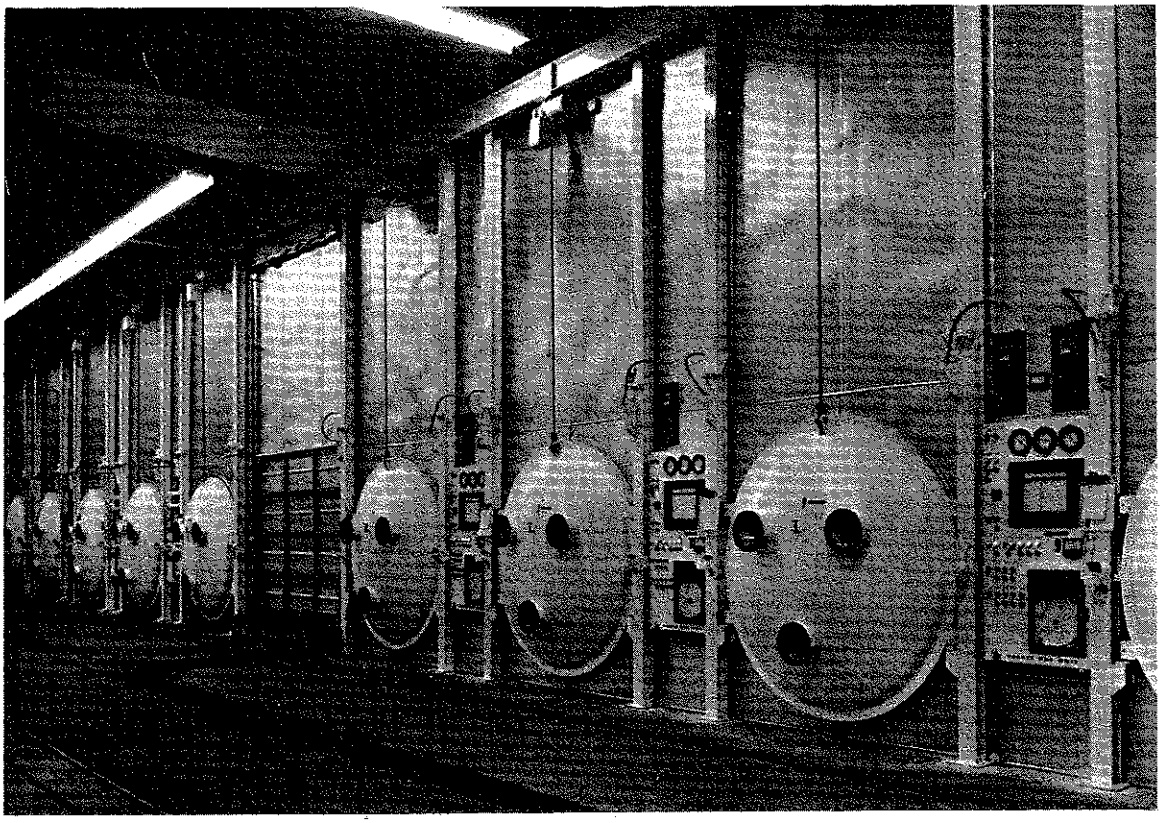

Fig. 3. Installation for freeze drying food, 1967 (courtesy of Oregon Freeze Dry Foods, Inc.).

of sublimation of ice. Unpublished data from the U. S. Army Natick Laboratories reveal that high-quality freeze dried foods can be prepared by a single-stage freeze drying operation. When the drying vessel containing chilled silica gel is held under refrigeration, it is unnecessary to use a vacuum even though dehydration at atmospheric pressure takes more than twice as long as dehydration in a vacuum. Using predetermined ratios of silica gel to sample makes drying to moisture levels up to 10 percent feasible. In conventional freeze drying procedures, moisture levels of more than 4 percent usually represent a relatively dry surface and a wet core. Freeze drying with silica gel does not require costly or sophisticated equipment. A refrigerated room, a vacuum pump, and an oven in which to dry the used silica gel are the major requirements.

FREEZE DRIED FOODS

All methods of drying provide reliable protection against microbiological deterioration, together with a reduction in weight corresponding to the initial water content. Freeze drying eliminates or minimizes the undesirable changes of historic drying procedures and provides for the rapid restoration of food to its prefrozen condition. This rapid reversibility places precooked and ready-to-eat freeze dried items in the category of convenience foods. Military experience with Long Range Patrol Food Packets provides assurance that virtually all precooked stews and casserole items can be reconstituted with hot water in less than 5 minutes to yield highly acceptable meal items heated to serving temperature. This is less time than is required for heating corresponding canned items and substantially less than for frozen products. A variety of freeze dried patties and other deep-fat fried items rehydrate with hot water in a matter of seconds without losing their crisp, freshly fried surface texture. Freeze dried cottage cheese and familiar salads like chicken, tuna, or egg reconstitute to normal products in less than 5 minutes with water at room temperature. The convenience status of freeze dried foods which require both rehydration and cooking is marginal. Raw steaks, chops, hamburger, fish fillets, shrimp and many raw vegetables require about 15 minutes for reconstitution and the same cooking time as their fresh counterparts.

With a few limitations, which will be noted, most foods are receptive to freeze drying. Structureless foods such as fruit juices, milk, and raw scrambled eggs are generally dried by procedures other than freeze drying. Practical considerations preclude the freeze drying of food masses which exceed three-fourths inch

in thickness, although no limitation is placed on the other dimensions. Since freezing is a prerequisite for freeze drying, no attempt has been made to process items such as lettuce, tomatoes, and melons, which are damaged by freezing. To date, cured meats such as ham have not proved stable enough during prolonged storage to justify freeze drying. Emulsion-type sausage such as the frankfurter is not freeze dried owing to poor rehydration and to leakage of fat during storage at room temperature. Bakery items such as bread have been freeze dried but are not rehydrated by the immersion procedures used on other products.

Meryman (*28*) points to the paradoxical situation that most labile biochemicals, even living organisms, can be stabilized by freeze drying, but this success is not duplicated with food. Damage may occur during freezing, drying, storage, and reconstitution. Such damage, which is cumulative, becomes apparent when the rehydrated product is eaten. The commercial freezing of foods for subsequent drying is essentially the same as for the frozen food market. This operation is not regarded as a significant source of damage.

Several types of damage may occur during the freeze drying operation. Thawing of the food surface results in foam, which collapses on the surface as a film that retards drying and subsequent rehydration. Loss of water-holding capacity, resulting in dryness and toughness, is perhaps the most frequently observed damage associated with freeze drying, particularly in muscle. This type of change has been related to exposure to excessive temperature during drying (*23*). In protein foods such exposure results in increased cross binding. In the case of shrimp an excessive drying temperature may cause color deterioration during storage (*23*). Changes affecting both water-holding capacity and flavor may also be caused by browning reactions of the carbonyl-amine type during prolonged drying at elevated temperature. Loss or alteration of volatile flavor may occur during the drying operation, especially with fruits. In fatty foods such as pork, excessive temperature during drying results in "leakage" of fat, which is distributed over the dried surfaces. This increases the potential for rancidity during storage and for water repellency at the time of rehydration.

In great measure, however, damage during freeze drying can be minimized or avoided by adherence to recognized operating procedures. According to MacKenzie and Luyet (*26*) avoidance of denaturation and loss of protein solubility of beef requires conditions substantially milder than currently applied in commercial production. Since such changes also result from cooking, they do not interfere with acceptance of the beef, according to panel tests.

Most of the deterioration in the quality of freeze dried foods occurs during storage (*23*). It has long been recognized that nonenzymatic browning is a major cause of deterioration during storage. This reaction leads to the development not only of a red-brown color, but also of unpalatable flavors and of a decreased capability to absorb and retain water. In the case of beef this last change results in a hard, dry, spongy texture. The browning reaction is strongly accelerated by temperature, $Q_{10} = 4$ (*21*) and by moisture concentration with maximum activity in the 5 to 8 percent range. Experience with a variety of foods has demonstrated that a moisture level of 2 percent is generally adequate for the control of browning. Many foods adsorb water vapor so rapidly that exposure to atmospheric humidity must be avoided while the food is being packaged after drying (*3*).

Notwithstanding the difficulties of quantitative interpretation, evidence (*3*) decisively indicts gaseous oxygen as causing adverse changes in the odor and flavor of many freeze dried foods. Since oxygen is responsible for the rancidity of lipid components, it is suspected that carbonyl compounds formed by such oxidative processes react with protein materials to produce adverse changes in texture. Although rancidity requires a substantial induction period, the phospholipid fraction of freeze dried animal tissue exhibits an immediate and active uptake of oxygen, which results in odors variously described as fishy, stale, and putrid. Furthermore, oxygen is known to destroy carotenoids, heme pigments, the astacene pigment of shrimp, ascorbic acid, and a number of other biological materials.

The known deteriorative changes associated with either oxygen or moisture emphasize the need for reliable containers for freeze dried foods. Current commercial methods make it unfeasible to require an oxygen concentration of less than 2 percent in the headspace gas in containers of freeze dried food, but experience with many foods has shown that concentrations of far less than 2 percent are necessary to suppress oxidative changes. Hope is held for reducing headspace oxygen to a few thousandths of one percent by use of a palladium catalyst in conjunction with flushing the container with a mixture of nitrogen and hydrogen (*1*).

All freeze dried foods probably could resist adverse changes during storage if they were not exposed to either atmospheric oxygen or humidity. A major engineering innovation is needed to permit the transfer of the dry product from a drying chamber to a container without exposure to the atmosphere.

THE FUTURE

Freeze dried foods have had but a brief history: only a small fraction of the food industry has experimented with their production or their development for the market, and a still smaller fraction of the consuming population has gained an insight into their use and properties. Several freeze dried foods, however, are already estab-

lished in the market, primarily the institutional market, and others have reached the test stage. A number of convenience items such as fully prepared freeze dried stews and casserole items, which can be rehydrated and served hot within 5 minutes, are worthy candidates for the marketplace.

Improvements in the quality and performance of freeze dried foods, especially after prolonged storage, together with lowered production cost, are essential for a strong market position. This is particularly true in the United States and other countries which have a well-developed frozen food industry with adequate facilities for transport and storage between the factory and the site of consumption.

From the standpoint of calories and nutrients, dehydration is equivalent to concentration through removal of noncaloric weight. Upon addition of water, freeze dried food undergoes a rapid transition from the preserved-concentrated state to the form in which it is normally consumed. The combination of preservation, concentration with rapid reversibility, storage stability, and acceptability accounts for the attractiveness of freeze dried foods for military feeding systems. These same characteristics are applicable to campers and hikers.

While drying reduces the weight of food to a minimum, freeze drying does not achieve a significant reduction in volume. It has been found however that most freeze dried foods when properly plasticized can be compressed without serious fragmentation. Moreover, for many products this compression is reversible. When immersed in water the compressed product rehydrates and is restored to its original, prefrozen form and shape. This advantage is exhibited by a number of freeze dried products such as ground and diced beef, diced chicken, shrimp, meat balls, pork sausage, corn, peas, beans, and a number of stews and casseroles. The principal group of foods which fail to exhibit reversible compression are sugar-containing fruits such as strawberries and peaches. Figure 4 illustrates 20 grams of freeze dried peas before and after compression and after rehydration.

As a generalization many freeze dried foods have a bulk density of around 0.3 gram/cc. On the basis of current technology it appears feasible to compress to a bulk density of 0.8 to 0.9 without impairing reversibility (*4*). Not only has a reduction to three eighths or one third of the precompression volume been achieved, but there is a significant improvement in the ratio of food to inedible packaging material. Exploiting the reversibility of freeze dried foods from both compression and dehydration makes it technically feasible to prepare compressed food bars which under stress conditions may be eaten directly from the compressed state; however, under other conditions the same compressed bar may be rehydrated to yield a familiar meal item of high acceptability. With such technology it is possible to prepare a whole meal from reversible compressed freeze dried shrimp cocktail, cream of mushroom soup, beef stew, Waldorf salad, and chocolate custard. These components for a meal of 1,200 Kcal. would weigh approximately 1 pound and occupy a volume of 22 cubic inches. The potential utility

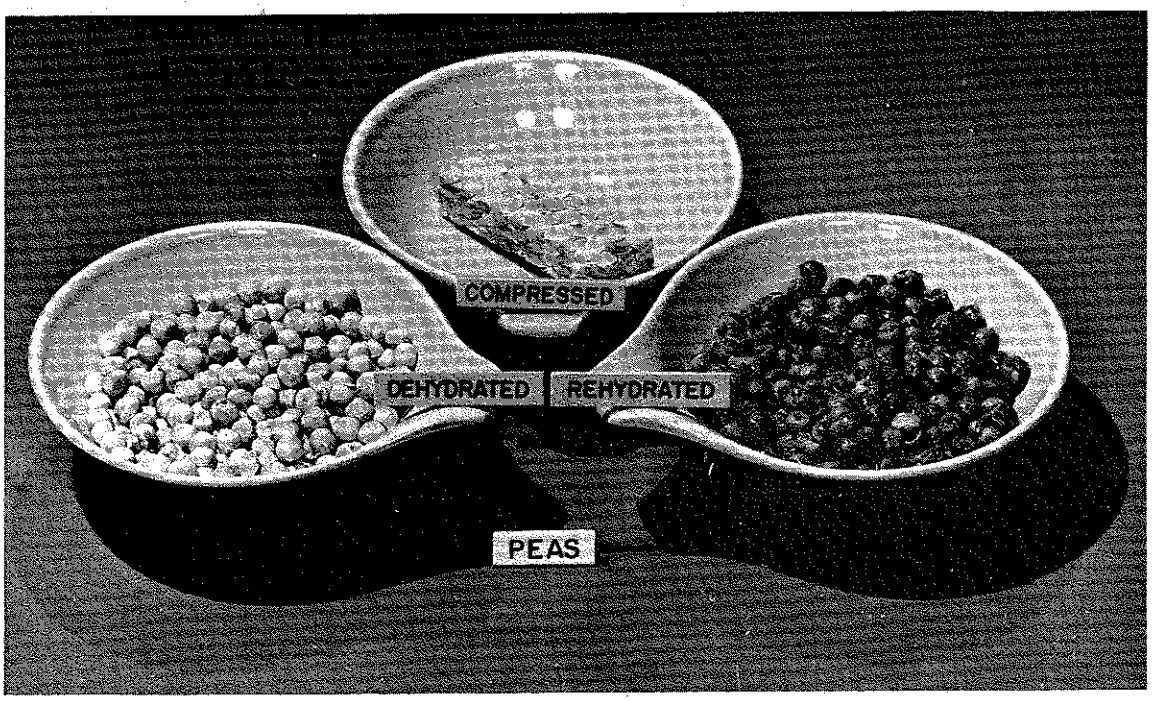

Fig. 4. Freeze dried peas before and after compression and after rehydration from the compressed state.

of this technology for military feeding systems is apparent, and it is probable that products of such technology will find outlets in the civilian economy.

Before World War II freeze drying was an obscure laboratory process for preserving bacterial cultures and immunological reagents. Freeze drying proved its commercial feasibility through the blood plasma program of World War II and then successfully met the challenging requirements of the critical years which established a vigorous penicillin industry. Freeze drying is now gaining specialized bases in the highly competitive food industry. These gains reflect advances in the equipment and in the process that permit the development of food items which fulfill special needs. The unique features of freeze dried foods provide a rational basis for continued growth.

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